

PROCESS TO MAKE A SULPHUR CONTAINING STEAM CRACKER
FEEDSTOCK

Field of the invention

The invention is directed to a process to make a sulphur containing steam cracker feedstock from natural gas by combining a paraffinic feedstock as obtained in a Fischer-Tropsch process and a sulphur containing feedstock from another source.

Background of the invention

It is well known to the skilled person in the technical field of steam cracker processes to add sulphur to the feed in order to reduce coke formation. The coke formation in steam cracker furnace tubes is principally formed through two mechanisms, pyrolysis reactions and catalytic dehydrogenation reactions. The pyrolysis reactions are minimized by using low operating pressure, having high steam-to-hydrocarbon ratios, on the order of 30% to 60%, and avoiding excessive tube metal temperatures and the possibility of allowing unvaporized feed into the high temperature zones. In order to withstand high tube metal temperatures, up to 2100 °F, alloys containing high nickel and chromium are used, for instance 35% nickel and 25% chrome. These metals catalyze dehydrogenation reactions and therefore need to be passivated. Sulfiding is the typical solution for passivation. It is a common practice for steam cracker operators to inject coke inhibitors right after the decoking operation. That is when the tube wall metal catalyzing activities are highest. Before the hydrocarbon

feedstock is fed into the furnace, DMS or DMDS is injected into the coil with steam to form a sulfide film. For a typical liquid feedstock, the sulfur content in the feedstock usually is sufficient to maintain the sulfide level during the actual steam cracking process. Sulphur may be added to the feed if there is not already enough sulfur in the feed. In this case, perhaps 20 ppm to 100 ppm of sulfur is added to minimize the coke and CO production.

It is also well known to use the naphtha paraffin product as obtained in a Fischer-Tropsch process as steam cracker feedstock. For example "The Markets for Shell Middle Distillate Synthesis Products", Presentation of Peter J.A. Tijm, Shell International Gas Ltd., Alternative Energy '95, Vancouver, Canada, May 2-4, 1995 on page 5 it is mentioned that SMDS naphtha, the Fischer-Tropsch derived naphtha fraction of the Shell MDS process, is used as steam cracker feedstock in for example Singapore.

Because a Fischer-Tropsch derived product contains almost no detectable levels of sulphur, sulphur will have to be added to this feedstock before it can be used as steam cracker feedstock. This may be done by adding a sulphur additive like dimethyl disulfide (DMDS) or by blending the Fischer-Tropsch feed with a high sulfuric content material as described in more detail in 'Preliminary Survey on GTL Business Based on SMDS technology, June 2001, Japan External Trade Organization (JETRO), section 6.2.3.

Adding sulphur to a Fischer-Tropsch derived feed in a steam cracker process is also described in a more recent patent publication US-A-2003/0135077. This publication

describes the production of a low sulphur Fischer-Tropsch derived naphtha at a remote location, transporting this product to a steam cracker location and adding a sulphur compound to the naphtha before using said naphtha as steam cracker feed.

WO-A-9937736 discloses a process wherein a field condensate as separated from raw natural gas is hydrotreated to reduce the sulphur level. According to this publication sulphur needs to be removed in order to use it as fuels or for blending with other hydrocarbons and as raw materials for chemical processes.

A disadvantage of the process according to WO-A-9937736 is the fact that additional hydroprocessing units are required.

Summary of the invention

The object of the present invention is to make a sulphur containing steam cracker feedstock from natural gas.

This object is achieved by the following process.
Process to make a sulphur containing steam cracker feedstock from crude natural gas by performing the following steps:

- (a) separating a sulphur containing liquid field condensate fraction from the natural gas,
- (b) further separating a sulphur containing fraction comprising hydrocarbon compounds having 3 or more carbon atoms from the natural gas to obtain a plant condensate,
- (c) preparing a mixture of carbon monoxide and hydrogen from the gas obtained in step (b),
- (d) preparing a paraffin product by performing a Fischer-Tropsch reaction using the carbon monoxide and hydrogen from step (c), and

(e) combining the paraffin product or part of said product with the sulphur containing fraction comprising hydrocarbon compounds having 3 or more carbon atoms obtained in step (b) to obtain the sulphur containing steam cracker feedstock having a sulphur.

Applicants have found that with the process according to the invention part of the C3+ compounds as obtained separated from the natural gas can be advantageously be combined with the paraffin product as obtained in the Fischer-Tropsch process. Applicants found that this stream may contribute to the volume of steam cracker feedstock and to its sulphur content, thereby making it an excellent steam cracker feed meeting specifications for direct use. This is advantageous because it saves tankage facilities at the production site of the Fischer-Tropsch process and one product can be shipped to the overseas client instead of two separate products.

Detailed description of the invention

Step (a) may be performed according to well known processes. Typically the natural gas is won from subterranean wells. The gaseous hydrocarbons of 1 to 5 carbon atoms are typically separated from the C5+ hydrocarbons after the gas reaches the surfaces, for example in so-called slug catchers. The liquid product so obtained is also referred to as field condensate and may have very high sulphur levels, for example above 1500 ppm and even above 1900 ppm. The typical lower level is 1000 ppm sulphur. The natural gas wherein field condensate is separated will be referred to as pre-cleaned natural gas.

This liquid condensate as obtained in step (a) may have a very high final boiling point, even above 300 °C,

while at the same time the majority of the products boils below 300 °C. By preferably separating off the high boiling fraction, by for example a flashing step or a distillation step, a lower boiling fraction containing sulphur compounds and meeting the boiling range requirements for usage as steam cracker feedstock. This fraction does not need further desulphurisation treatments in order to be used in a preferred embodiment of the present invention as additional blending component in step (e) to prepare a steam cracker feedstock. Preferably this low boiling fraction as isolated from the field condensate has a final boiling point of between 120 and 230 °C, and more preferably between 140 and 215 °C. The initial boiling point corresponds with the C₅ hydrocarbons still present in the liquid field condensate. The final boiling point of the low boiling fraction may vary depending on the sulphur content in the field condensate, the blending ratio of the fractions obtained in steps (b) and (a) and the Fischer-Tropsch product in step (e) and the desired sulphur level of the resultant mixture. An optimal operation may be determined using ordinary skills. The higher boiling fraction which is rich in sulphur compounds and organic acids, may be further processed in so-called local condensate refineries. The low boiling fraction preferably contains between 200 and 6000 ppm sulphur.

Prior to performing step (b) the majority of the sulphur is separated from the pre-cleaned natural gas as obtained in step (a) by various possible techniques. Preferably sulphur is removed from the natural gas by so-called absorbent type processes. These well known processes include a step wherein the natural gas is

contacted with a liquid mixture which contains a physical and a chemical absorbent. In such a process the gas mixture is treated at superatmospheric pressure in two steps consecutively with two different liquid mixtures which contain a physical absorbent and a chemical absorbent. Typical chemical absorbents are tertiary amines, particularly tertiary amines which contain at least one hydroxyalkyl group. Triethanol amine, diethyl ethanol amine (DEMEA), and methyl diethanol amine (MDEA) are very suitable. Typical physical absorbents are propylene carbonate N-methyl pyrrolidone, dimethyl formamide, dimethyl ether of polyethylene glycol, tetraethyleneglycoldimethylether and sulfolane are very suitable. Examples of such processes are described in detail in US-A-4372925 and in textbooks such as Gas Purification, 5th ed./Arthur Kohl and Richard Nielsen, 1997, Gulf Publishing Company, ISBN 0-88415-220-0 Chapter 1.

In step (b) hydrocarbon compounds having 3 or more carbon atoms are separated from the natural gas prior to converting the gas to synthesis gas. Preferably separation is performed by cooling the gas to a temperature and pressure conditions at which these hydrocarbons liquefy. The liquid products may then be easily separated from the gas. Cooling may preferably be performed by indirect heat exchange against liquid nitrogen. Liquid nitrogen may preferably be the excess nitrogen as obtained when separating air to obtain purified oxygen for use in step (c). A more preferred method is by lowering the pressure, separating the condensed C₃+ hydrocarbons, and optionally increasing the pressure level before making use of the gas to prepare

synthesis gas. Preferably the gas is lowered from a pressure exceeding 50 bars to a pressure below 40 bars, preferably below 30 bars. After separation of the liquid hydrocarbons, the pressure of the gas is increased to a level above 50 bars, preferably between 50 and 80 bars. The C₃ and C₄ hydrocarbons thus obtained may be blended with the LPG product as isolated from the product prepared in step (d).

The synthesis gas to be used for the Fischer-Tropsch reaction is made in step (c) from the gas obtained in step (a) by partial oxidation and/or steam/methane reforming.

To adjust the H₂/CO ratio in the synthesis gas, carbon dioxide and/or steam may be introduced into the partial oxidation process. The H₂/CO ratio of the synthesis gas is suitably between 1.3 and 2.3, preferably between 1.6 and 2.1. If desired, (small) additional amounts of hydrogen may be made by steam methane reforming, preferably in combination with the water gas shift reaction. The additional hydrogen may also be used in other processes, e.g. hydrocracking.

In another embodiment the H₂/CO ratio of the synthesis gas obtained in the catalytic oxidation step may be decreased by removal of hydrogen from the synthesis gas. This can be done by conventional techniques as pressure swing adsorption or cryogenic processes. A preferred option is a separation based on membrane technology. Part of the hydrogen may be used in the hydrocracking step of especially the heaviest hydrocarbon fraction of the Fischer-Tropsch reaction.

The synthesis gas obtained in the way as described above, usually having a temperature between 900 and 1400 °C, is cooled to a temperature between 100 and 500 °C, suitably between 150 and 450 °C, preferably between 300 and 400 °C, preferably under the simultaneous generation of power, e.g. in the form of steam. Further cooling to temperatures between 40 and 130 °C, preferably between 50 and 100 °C, is done in a conventional heat exchanger, especially a tubular heat exchanger. To remove any impurities from the synthesis gas, a guard bed may be used. Especially to remove all traces of HCN and/or NH₃ specific catalysts may be used. Trace amounts of sulphur which may still be present in the gas used in step (c) may be removed by an absorption process using iron and/or zinc oxide.

The purified gaseous mixture, comprising predominantly hydrogen, carbon monoxide and optionally nitrogen, is contacted with a suitable catalyst in the catalytic conversion stage, in which the normally liquid hydrocarbons are formed.

The catalysts used for the catalytic conversion of the mixture comprising hydrogen and carbon monoxide into hydrocarbons in step (d) are known in the art and are usually referred to as Fischer-Tropsch catalysts. Catalysts for use in this process frequently comprise, as the catalytically active component, a metal from Group VIII of the Periodic Table of Elements. Particular catalytically active metals include ruthenium, iron, cobalt and nickel. Cobalt is a preferred catalytically active metal in view of the heavy Fischer-Tropsch hydrocarbon which can be made. As discussed before, preferred hydrocarbonaceous feeds are natural gas or

associated gas. As these feedstocks usually results in synthesis gas having H_2/CO ratio's of about 2, cobalt is a very good Fischer-Tropsch catalyst as the user ratio for this type of catalysts is also about 2.

5 The catalytically active metal is preferably supported on a porous carrier. The porous carrier may be selected from any of the suitable refractory metal oxides or silicates or combinations thereof known in the art. Particular examples of preferred porous carriers include
10 silica, alumina, titania, zirconia, ceria, gallia and mixtures thereof, especially silica, alumina and titania.

 The amount of catalytically active metal on the carrier is preferably in the range of from 3 to 300 pbw per 100 pbw of carrier material, more preferably from 10
15 to 80 pbw, especially from 20 to 60 pbw.

 If desired, the catalyst may also comprise one or more metals or metal oxides as promoters. Suitable metal oxide promoters may be selected from Groups IIA, IIIB, IVB, VB and VIB of the Periodic Table of Elements, or the
20 actinides and lanthanides. In particular, oxides of magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, cerium, titanium, zirconium, hafnium, thorium, uranium, vanadium, chromium and manganese are very suitable promoters. Particularly preferred metal oxide
25 promoters for the catalyst used to prepare the waxes for use in the present invention are manganese and zirconium oxide. Suitable metal promoters may be selected from Groups VIIB or VIII of the Periodic Table. Rhenium and Group VIII noble metals are particularly suitable, with
30 platinum and palladium being especially preferred. The amount of promoter present in the catalyst is suitably in the range of from 0.01 to 100 pbw, preferably 0.1 to 40,

more preferably 1 to 20 pbw, per 100 pbw of carrier. The most preferred promoters are selected from vanadium, manganese, rhenium, zirconium and platinum.

5 The catalytically active metal and the promoter, if present, may be deposited on the carrier material by any suitable treatment, such as impregnation, kneading and extrusion. After deposition of the metal and, if appropriate, the promoter on the carrier material, the loaded carrier is typically subjected to calcination. The
10 effect of the calcination treatment is to remove crystal water, to decompose volatile decomposition products and to convert organic and inorganic compounds to their respective oxides. After calcination, the resulting catalyst may be activated by contacting the catalyst with
15 hydrogen or a hydrogen-containing gas, typically at temperatures of about 200 to 350 °C. Other processes for the preparation of Fischer-Tropsch catalysts comprise kneading/mulling, often followed by extrusion, drying/calcination and activation.

20 The catalytic conversion process may be performed under conventional synthesis conditions known in the art. Typically, the catalytic conversion may be effected at a temperature in the range of from 150 to 300 °C, preferably from 180 to 260 °C. Typical total pressures
25 for the catalytic conversion process are in the range of from 1 to 200 bar absolute, more preferably from 10 to 70 bar absolute. In the catalytic conversion process especially more than 75 wt% of C₅+, preferably more than 85 wt% C₅+ hydrocarbons are formed. Depending on the
30 catalyst and the conversion conditions, the amount of heavy wax (C₂₀+) may be up to 60 wt%, sometimes up to 70 wt%, and sometimes even up till 85 wt%. Preferably a

cobalt catalyst is used, a low H_2/CO ratio is used (especially 1.7, or even lower) and a low temperature is used (190-240 °C), optionally in combination with a high pressure. To avoid any coke formation, it is preferred to use an H_2/CO ratio of at least 0.3. It is especially preferred to carry out the Fischer-Tropsch reaction under such conditions that the ASF-alpha value (Anderson-Schulz-Flory chain growth factor), for the obtained products having at least 20 carbon atoms, is at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955. Preferably the Fischer-Tropsch hydrocarbons stream comprises at least 40 wt% C_{30+} , preferably 50 wt%, more preferably 55 wt%, and the weight ratio C_{60+}/C_{30+} is at least 0.35, preferably 0.45, more preferably 0.55.

Preferably, a Fischer-Tropsch catalyst is used, which yields substantial quantities of paraffins, more preferably substantially unbranched paraffins. A most suitable catalyst for this purpose is a cobalt-containing Fischer-Tropsch catalyst. Such catalysts are described in the literature, see e.g. AU 698392 and WO-A-9934917.

The Fischer-Tropsch process may be a slurry FT process or a fixed bed FT process, especially a multitubular fixed bed.

The paraffin product may be isolated from the product as obtained in step (d) directly by means of distillation. Preferably such a fraction is first hydrogenated in order to remove any olefins and oxygenated compounds that could negatively influence the properties of the resulting blend for use as steam cracker feedstock. The paraffin product may also be

isolated from the effluent of a hydrocracking step as performed on the entire or part of the product as obtained in step (d). Such a paraffin product will comprise a larger content of iso-paraffins. Preferably the iso to normal ratio of the paraffins in the paraffin product is less than 0.5, preferably less than 0.3.

The paraffin product comprises preferably more than 90 wt% of C₅ to compounds boiling at 370 °C. More preferably the paraffin product boils in the naphtha range, preferably comprising for more than 90 wt% compounds starting from C₅ and up to compounds boiling at 204 °C.

The paraffin product is combined in step (e) with the C₃ plus fraction or the C₅ plus fraction obtained in step (b). The weight ratio of step (d) product to step (b) product is preferably between 30:1 and 5:1. The resulting blend preferably has the following properties:

Specific Gravity of between 0.65 to 0.74,
Colour Saybolt of more than +20,
Unsaturation < 1 vol%,
Paraffin content of between 65% and 100 vol.%.
Iso-normal paraffin ratio of less than 0.5,
Sulphur content of between 50 and 650 ppm, preferably between 100 and 650 ppm,
Final boiling point of between 150 and 204 °C, and a Reid Vapour Pressure at 37.8 °C of not more than 13 psi.

The invention is also directed to the use of the blend as obtained by the process according to the present invention as a steam cracker feedstock to make lower olefins, especially propylene and/or ethylene.

Figure 1 illustrates the process according to the present invention. From a sour natural gas 11 a field condensate 12 is separated in a slug catcher 1. The field condensate 12 is separated in a separator 2 into a low boiling fraction 13 and a high boiling fraction 14. Fraction 14 is supplied to an optional condensate refinery. Sulphur is removed from the natural gas 15, which is poor in condensate, in a Sulfinol Unit 4. C₃+ hydrocarbons 17 are separated from the gas 16 poor in sulphur in separator unit 5. The hydrocarbons 17 are further split by distillation unit 6 in a C₃ and C₄ stream 19 and a stream 18 containing mainly C₅+ hydrocarbons.

The cleaned gas 20 is used in synthesis gas manufacturing unit 7 to obtain synthesis gas 21. This synthesis gas 21 is used as feedstock in the Fischer-Tropsch reaction step 8 in which a paraffinic product 22 is obtained. This product is separated into various fractions boiling below (fraction 23) and above (fractions 25 and 26) of the naphtha fraction 24. This naphtha fraction 24 is mixed with fractions 13 and 18 in mixing unit 10 to obtain a steam cracker feedstock 27 according to the present invention.

C L A I M S

1. Process to make a sulphur containing steam cracker feedstock from crude natural gas by performing the following steps:

(a) separating a sulphur containing liquid field

5 condensate fraction from the natural gas,

(b) further separating a sulphur containing fraction comprising hydrocarbon compounds having 3 or more carbon atoms from the natural gas to obtain a plant condensate,

10 (c) preparing a mixture of carbon monoxide and hydrogen from the gas obtained in step (b),

(d) preparing a paraffin product by performing a Fischer-Tropsch reaction using the carbon monoxide and hydrogen from step (c), and

15 (e) combining the paraffin product or part of said product with the sulphur containing fraction comprising hydrocarbon compounds having 3 or more carbon atoms obtained in step (b) to obtain the sulphur containing steam cracker feedstock having a sulphur content of between 50 and 1000 ppm.

20 2. Process according to claim 1, wherein step (b) is performed by cooling the gas to a temperature and pressure conditions at which the C3 and higher hydrocarbons liquefy.

25 3. Process according to claim 2, wherein cooling is performed by indirect heat exchange against liquid nitrogen.

4. Process according to claim 3, wherein the liquid nitrogen is obtained when separating air to obtain

purified oxygen for use in step (c) to prepare the mixture of carbon monoxide and hydrogen.

5 5. Process according to claim 2, wherein step (b) is performed by lowering the pressure, separating the condensed C₃+ hydrocarbons, and optionally increasing the pressure level before making use of the gas to prepare synthesis gas in step (c).

10 6. Process according to claim 5, wherein in step (b) the gas is lowered from a pressure exceeding 50 bars to a pressure below 40 bars.

7. Process according to claim 6, wherein the pressure is lowered to below 30 bars.

15 8. Process according to any one of claims 5-7, wherein after separation of the liquid hydrocarbons, the pressure of the gas is increased to a level of between 50 and 80 bars.

20 9. Process according to any one of claims 1-8, wherein from the fraction comprising hydrocarbon compounds having 3 or more carbon atoms a fraction of C₃ and C₄ hydrocarbons are isolated and blended with the LPG product as isolated from the product prepared in step (d) and wherein the remaining C₅+ hydrocarbons are used in step (e).

25 10. Process according to any one of claims 1-9, wherein the gas field condensate or part of said gas field condensate as isolated in step (a) is combined with the product as obtained in step (e).

30 11. Process according to any one of claims 1-10, wherein the paraffin product obtained in step (d) and used in step (e) comprises for more than 90 wt% compounds starting from C₅ and up to compounds boiling at 204 °C.

12. Process according to any one of claims 1-11, wherein the sulphur content of the steam cracker feedstock as obtained in step (e) is greater than 50, preferably > 100 ppm.

5 13. Process according to any one of claims 1-12, wherein the steam cracker feedstock as obtained in step (e) has the following properties:

Specific Gravity of between 0.65 to 0.74,

Colour Saybolt of more than +20,

10 Unsaturates < 1 vol %,

Paraffin content of between 65% and 100 vol.%,

Iso-normal paraffin ratio of less than 0.5,

Sulphur content of between 50 and 650 ppm,

Final boiling point of between 150 and 204 °C, and

15 Reid Vapour Pressure at 37.8 °C of not more than 13 psi.

14. Use of a blend as obtained by the process according to any one of claims 1-13 as a steam cracker feedstock to make propylene and/or ethylene.